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Synthesis and linear rheological property of comb-like styrene-based polymers with a high degree of branch chain

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ABSTRACT

A series of model comb-like polymers (PSVS-*g*-PS) with high branching degree were synthesized by nucleophilic substitution reaction between iodinated copolymer of styrene (St) with 4-(vinylphenyl)-1-butene (VSt) (PSVSI, backbone) and living polystyrene lithium (PSLi, side chain). This method is a facile way for modular synthesis of graft copolymers based on living anionic polymerization and hydrozirconation reaction. The branching density of PSVS-*g*-PS (the number of branch chain per 100 repeat backbone units) ranged from 2.4 to 20.7%. The backbone length of PSVS-*g*-PS was larger than the entanglement molecular weight (M_e) of PS, while the molecular weight of branch chain was designed to be below or above the M_e of PS. The results from the linear rheological properties of the PSVS-*g*-PS showed hierarchical relaxation process. One appeared in the intermediate angular frequency region, corresponding to the relaxation of the side chain. The other is in the terminal region, which is related to the movement of the whole comb polymer. From scaling law of zero shear viscosity (η_0) of PSVS-*g*-PS with versus molecular weight, it could be seen that the dynamical behavior of PSVS-*g*-PS was different from those of both poly(macromonomers) and entangled linear polymer chains, indicating that there is certain entanglement for PSVS-*g*-PS with long branch chain.

1. Introduction

The living polymerization techniques offer a variety of routes to tailor chemical composition, molecular weight and molecular weight distribution of resultant polymers, as well as chain molecular architecture [1–8]. Up to now, nonlinear polymers (such as star-like, hyper-branched, and comb-like polymers etc.) have been successfully synthesized, with investigation on their properties originated from their molecular architectures [7,9–16]. "Graft onto" method [17,18] is considered as a modular approach in the preparation of comb-like (or graft) (co)polymers. There have been many methods of this strategy to synthesize the well-defined graft copolymers for the past years, such as the coupling reaction between the living anionic polymer chain (side chain) and the alkyl halogen (Cl, Br) [1,18–21], epoxy group [22], and Si–Cl group [23–25] on the backbone, click reaction [26–29] between the branch and backbone, the coupling reaction between the appending β-keto ester and the terminal amine [30]. In our previous work, a facile method was developed to synthesize an almost fully hydroiodinated 1,2-polybutadiene (1,2-PB) via the hydrozirconation of 1,2-PB with controlled degree of halogenation and molecular weight of the resultant polymers [31]. At the same time, a series of well-defined comb-like (co)polymers have been synthesized by a very effective and fast nucleophilic substitution reaction between iodinated 1,2-polybutadiene (PB-I, backbone) and living polymer lithium (side chains) [17]. However, the degradation of 1,2-PB backbone will take place during hydrozirconation of 1,2-PB due to the presence of few 1,4-units in the 1,2-PB backbone when the backbone is larger than 6000 g/mol [31,32]. To synthesize comb-like polymers without suffering this problem using the above method, a backbone without inner double bond but with pendent double bond could be used as precursor, such as poly(4-(vinylphenyl)-1-butene) ((PVSt)) [31]. Because there is no double bond in the backbone of PVSt, the degradation of backbone does not take place during the hydrozirconation.

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The chain molecular architecture (such as star-type, H-type and comb-like structure) strongly affects chain motion in polymer melt and determines rheological properties of polymers. Thus it is valuable to study the relationship between molecular architectures and rheological properties of polymer. Comparatively the case of the comb-like polymers is more complicated, as both branch chain length and branching density show significant influences on the rheological property of comb-like polymers [33–42]. Therefore, the synthesis of well-defined comb-like polymers is very important to establish the relationship between molecular parameters and the rheological properties of comb-like polymers. However, comb-like and even star-type or H-type polymers are found to suffer from structural imperfections as determined by temperature gradient interaction chromatography (TGIC) [43,44]. Although the most accurate synthetic protocol (Such as anionic living polymerization) is used, steric hindrance leads to a variation of molecular structures, which cannot be discerned in size exclusion chromatography (SEC) as the effect is stronger in molar mass than in size. Thus TGIC is recently used as a powerful tool to study molecular structure of branched polymers, combined with accurate synthesis and modeling, which provide a stable basis for using rheology as a complementary tool in charactering a complex polymer [45,46].

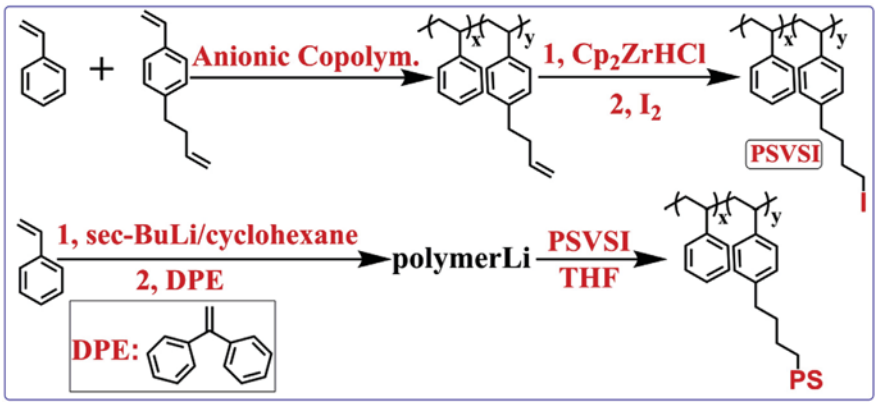
So far, the previous reports about the relationship between structural parameters and rheological properties of comb-like polymers are mainly focused on the samples with a low degree of branching (less than 100 branches per 10,000 carbon atom of the backbone) [34,36,41,47–58]. These comb-like polymers usually show hierarchical relaxations from the linear rheological result, in which the branch relaxes at first, and then the backbone relaxes after the glassy regions. Also, the linear rheological property of poly(macromonomer)s with densely branches (or bottlebrush) has been preliminarily studied for the last decade [35,59–65]. Some reports have showed that these poly(macromonomer)s remain unentangled due to too high branching density (~2000 branches per 10,000 backbone carbon atom), despite molecular weights of backbone and branch [63,65]. We wonder what will happen for the comb polymers with branching degree in the range of more than 100 branches per 10,000 backbone carbon atom but lower than that of poly(macromonomer)s. For this kind of comb polymers, the effects of the branch structure on the rheological properties for the comb polymers are still not well-understood due to the intricacy of this issue.

In this work, a series of model comb-like PSs with high branching degree (from more than 100 branches to 1000 branches per 10,000 backbone carbon atom) were successfully synthesized using our reported method. Here the copolymers of styrene (St) with 4-(vinylphenyl)-1-butene (VSt) (poly(St-*co*-VSt), abbreviated as PSVS) was chosen as the backbone precursor, the degradation of which does not take place during the hydrozirconation due to no double bond in the backbone. The incorporation of St into the backbone can reduce the spatial block for the nucleophilic substitution reaction between living PS chains and polyhalohydrocarbon (Scheme 1). At the same time, the backbones (PSVSI) with different iodinated degree were effectively synthesized by adjusting the molar ratio of VSt and St in order to synthesize comb-like copolymers with different branching densities. The influences of branched structure on the rheological property of the comb-like PSs were also explored. Although there is some uncertainty about the branching density between different backbones in the resultant comb-like copolymers, a qualitative result can be obtained according to the previous reports [45,46]. The presence of a small amount of impurity showed an influence in quantitative results but not in qualitative result. For this kind of comb-like copolymer, we are focused on qualitative behavior in this study. We wonder how the presence of branch chains with high branching density (different from bottlebrush polymers) affects the rheological properties of comb-like polymers.

2. Experimental part

2.1. Materials

Bis(cyclopentadienyl) zirconium dichloride (99%) and diisobutyl aluminum hydride (1 M in hexane) were purchased from Alfa Aesar. Vinylbenzyl chloride (VBC; Aldrich, 97%) and styrene (St; Aldrich, 99%) were dried with CaH_2 or NaH and distilled under reduced pressure prior to use. *sec*-butyllithium (*sec*-BuLi: 1.3 mol/L solution in cyclohexane/hexane (92/8)), *n*-butyllithium (*n*-BuLi: 1.6 mol/L solution in hexane) and allylmagnesiumchloride (AMC: 2.0 mol/L solution in tetrahydrofuran (THF)) were purchased from Aldrich and used as received. 1,1-Diphenylethylene (DPE) was purchased from Sigma–Aldrich, which was vacuum-distilled in the presence of butyllithium (BuLi) prior to use. Schwartz's reagent (Cp_2ZrHCl) was prepared using diisobutyl aluminum hydride and bis(cyclopentadienyl) zirconium dichloride in THF with yield 85% and stored in nitrogen-filled glovebox (used within 1 month) [66]. 4-(Vinylpheneyl)-1-butene (VSt) was prepared via the coupling reaction between AMC and VBC and distilled in the presence of phenylmagnesium chloride under reduced pressure before polymerization [67]. All the solvents (THF, cyclohexane, toluene) were distilled from sodium/potassium alloy with benzophenone. All oxygen- and moisture-sensitive manipulations were carried out under dry and oxygen free argon atmosphere using standard Schlenk techniques.



Scheme 1. Synthesis route for the comb-like PSVS-*g*-PS copolymers.

2.2. Synthesis

2.2.1. Synthesis of the backbone copolymer poly(St-co-Vst)

A series of poly(St-*co*-VSt)s ($PSVS_x$, here *x* represents the molar percentage of VSt in the copolymers) were prepared via the anionic copolymerization of VSt and St in toluene/THF (2/1 by volume) at −40 °C under argon atmosphere using *n*-BuLi as initiator [24]. After one hour, the system was quenched by the degassed methanol, and the copolymers were precipitated by pouring the solution into a large amount of methanol. The copolymers were vacuum-dried at 40 °C for more than 24 h.

2.2.2. Synthesis of the iodinated copolymer PSVSI

$PSVS_x$ was dissolved in THF and stirred overnight in N_2 filled Mbraun glovebox. Cp_2ZrHCl powder was added and vigorously stirred in the flask under argon atmosphere. The solution became dark red after all the powder dissolved in almost one hour at 35 °C, and then the iodine was slowly added to the previous solution for iodination reaction at −20 °C. The mixture was stirred for 1 h, and drops of degassed methanol were added to finish the reaction. After concentration by rotary evaporator, the viscous product was washed with methanol and purified by dissolve-precipitation using THF/methanol for 3–5 cycles. Isolated iodinated copolymers ($PSVSI_x$, here *x* represents the molar percentage of iodinated VSt in the resultant copolymers) were in ca.85% yield after dried under vacuum at 40 °C overnight.

2.2.3. Synthesis of the comb-like graft copolymers PSVS-g-PS

Living anionic polymerization of styrene (in cyclohexane) was carried out in N_2 filled Mbraun glovebox or by standard Schlenk techniques at room temperature, initiated by *sec*-BuLi, and then 1,1-diphenylethylene was added for capping affording PSLi. In order to maintain the same side chain length for each comparative experiment, a reservoir of living polymer was synthesized and stored, and aliquot of solution was used for a certain coupling reaction. Drops of living polymer solution were quenched for size exclusion chromatography (SEC) characterization before coupling reaction. The THF solution of $PSVSI_x$ (typically, 0.1 g/mL) was added to pre-designed living polymers solution (the amount of living polymer was determined according to the use of *sec*-BuLi, typically, 13 mmol/L) and violently stirred. After 0.5 h, the reaction was terminated by drops of degassed isopropanol. The resultant products (comb-like polymers) were precipitated in methanol and dried under vacuum at 60 °C. Methanol was dropwise added to polymer toluene solution (1 wt%) for precipitation fractionation experiment. The synthesized comb-like graft copolymers were described by the following nomenclature PSVS*x*-*y*-PS*z*, where *x* was the number-average molecular weight of backbone (kg/mol), *y* was the branching density of branch chains (the average number of side chains per 100 repeating units of the backbone), *z* was the number-average molecular weight of branch chains (kg/mol).

2.3. Characterization

^{1}H NMR spectra were performed on a Bruker AV 400 MHz spectrometer by using $CDCl_3$ as a solvent at room temperature. The absolute molecular weight of the backbone, side chain, and comb polymers was determined by SEC-MALLS (multiangle laser light scattering) at 35 °C using THF as an eluent with a flow rate of 1 mL/min. The SEC-MALLS consisted of a Model 1500 Digital HPLC pump, a DAWN HELEOS II (Wyatt multi-angle LS detector, GaAs 662.0 nm) and an Optilab T-rEX (Wyatt RI detector, LED light 658.0 nm). This instrument had a protected MZ-Gel SD *plus* 50 × 0.8 mm column (10^2 Å pore size) and two MZ-Gel SD *plus* 300 × 8.0 mm columns (10^3 and 10^5 Å pore size). The concentration of samples was about 0.5 mg/mL. The dn/dc values were measured by an Optilab T-rEX (Wyatt RI detector, LED light 658.0 nm) through six different concentrations of polymer solution with a flow rate of 1 mL/min. Data acquisition was performed using Wyatt Technology WinAstra6 software. The polydispersity index (PDI) of samples was determined by gel permeation chromatography (GPC) on TOSOH HLC 8220 GPC with two TSKgel SuperMultiporeHZ-M 150 × 4.6 mm columns (4 um particle size) using THF as an eluent against linear polystyrene standards. The samples with the concentration of 0.5 mg/mL were analyzed in THF at 40 °C with a flow rate of 1 mL/min. Glass transition temperature (T_g) of polymers was determined by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 instrument operating at a heating rate of 10 °C/min from 25 to 180 °C under a nitrogen atmosphere.

Rheological experiments were performed on an ARES-G2 rheometer (TA Instruments) with 25 mm parallel plate. Strain sweep experiments were performed first to determine the linear strain regime. Oscillatory frequency sweep was performed from 0.05 to 500 rad/s with a strain in the linear strain regime. Strain sweep and linear frequency sweep were performed at different temperatures ranged from 120 to 190 °C. Time–temperature superposition was used for the frequency sweep results of the comb-like copolymers, and the reference temperature was 150 °C. After the rheological measurements, there is any chain decomposition (or scission) of the graft copolymers (Fig. S1 in the Supporting Information).

3. Result and discussion

3.1. Synthesis of poly(St-co-VSt) backbone copolymer (PSVS)

Scheme 1 shows synthesis route for the comb-like copolymers PSVS-*g*-PS. Copolymerization of St and VSt is performed under variable feed ratios to prepare the backbone precursor ($PSVS_x$) with different compositions. In this work, the $PSVS_x$ copolymers with 3.8 and 31.4 mol% of VSt are synthesized, and they are termed as $PSVS_{3.8}$ and $PSVS_{31.4}$, respectively. The double bond on the side chain of the $PSVS_x$ backbone will be turned into branching points after hydrozirconation and iodinated reaction. The number of branching points can be controlled by the feed ratio of two monomers. The quantitative presence of the unreacted 1-butene type C=C double bond (C**H**$_2$=CH-, 5.1 ppm; CH$_2$=C**H**-, 5.8 ppm) was verified by ^{1}H NMR (Fig. 1a, $PSVS_{31.4}$ as an example). As shown in Fig. 2a, the obtained $PSVS_x$ possess a controlled molecular weight and a very narrow molecular distribution. The SEC-MALLS results for $PSVS_{31.4}$ and $PSVS_{3.8}$ are summarized in Table 1.

3.2. Synthesis of the iodinated copolymer PSVSI

Generally iodinated groups possess a very high reactivity to nucleophilic reagents, including the anionic living polymers. Thus the iodinated PSVS copolymers ($PSVSI_x$) are synthesized by the hydrozirconation of the pendent double bond and subsequent halogenolysis. It is very convenient to incorporate iodine atom due to the formation of grafting site with totally anti-Markovnikov fashion by hydrozirconation reaction. Fig. 1b presents the 1H NMR spectrum of $PSVSI_{23.1}$ (as an example). Comparing this spectrum with that of its precursor $PSVS_{31.4}$ (Fig. 1a), the peaks due to C**H**$_2$=C**H**– disappear completely, and the peaks corresponding to the iodine atom emerge quantitatively. Therefore, the butenyl group of $PSVS_x$ is completely reacted. In addition, an unexpected peak (at 0.9 ppm) is also observed, which is assigned to protons from hydrogenated unit [15,31]. It is inferred that the resultant polymer is a kind of ternary copolymers of St, 1-(vinylpheneyl)-butane and 1-(vinylpheneyl)-4-iodobutane. The formation of

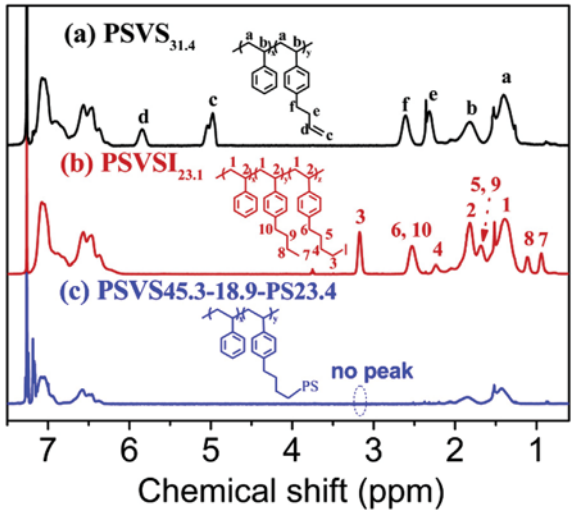


Fig. 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of (a) $PSVS_{31.4}$ (31.4 mol% VSt in the PSVS), (b) $PSVSI_{23.1}$ (23.1 represents the molar percentage of iodinated VSt in the resultant copolymers in the PSVSI), and (c) PSVS45.3-18.9-PS23.4 (A typical sample consisting of the backbone $PSVS_{31.4}$ with M_n = 45.3 kg/mol, side chain PS with M_n = 23.4 kg/mol, and graft density of 18.9 per 100 repeating units of the backbone).

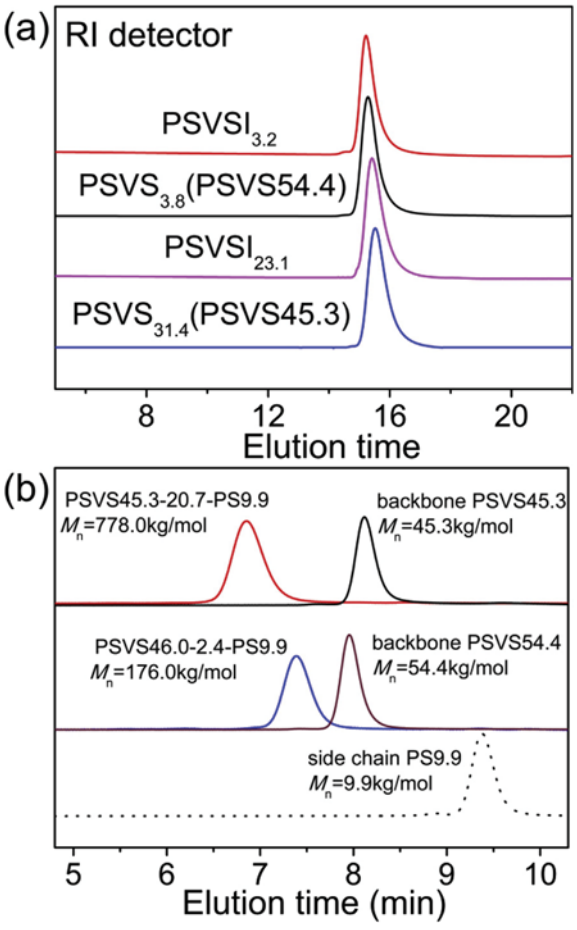


Fig. 2. (a) SEC-MALLS traces by the RI detector of $PSVS_x$ and iodinated PSVS ($PSVSI_x$) and (b) GPC traces against the linear polystyrene standards of backbone $PSVS_x$, side chain PS and fractionated comb-like copolymers PSVS-*g*-PS.

Table 1
Molecular structure parameters of the backbone, side chains and graft copolymers.

Sample	M_n[a] (kg/mol)	PDI[b]	dn/dc (mL/g)	Branching density[c] (%)	n_{br}[d]	ϕ_{br}[e]	T_g[f] (°C)
$PSVS_{31.4}$	45.3	1.03	0.158				68.4
$PSVS_{3.8}$	54.4	1.03	0.162				89.8
$PSVSI_{23.1}$	55.6	1.04	0.182				
$PSVSI_{3.2}$	57.1	1.04	0.179				
PS9.9	9.9	1.01	0.172				95.5
PS23.4	23.4	1.02	0.172				100.7
PSVS45.3-20.7-PS9.9	778.0	1.05	0.177	20.7	74.0	0.99	101.1
PSVS54.4-2.4-PS9.9	176.0	1.03	0.178	2.4	12.3	0.67	101.0
PSVS45.3-18.9-PS23.4	1698.0	1.03	0.179	18.9	70.6	0.99	103.7
PSVS54.4-2.5-PS23.4	357.1	1.04	0.184	2.5	12.9	0.85	104.8

[a] By SEC-MALLS in THF.
[b] By GPC based on linear polystyrene standards.
[c] The average number of branch chains per 100 repeating units of the backbone.
[d] The branch number per graft copolymer macromolecule.
[e] Volume fraction of the branches.
[f] By the DSC.

butane structural unit is attributed to hydrolysis (with methanol in workup) of residual alkylzirconium from incomplete halogenolysis. The iodinated degree is calculated from the peak area at 3.2 ppm (corresponding to the $-CH_2CH_2CH_2C\mathbf{H_2}I$) and 0.9 ppm (corresponding to $-CH_2CH_2CH_2C\mathbf{H_3}$), respectively. For $PSVS_{31.4}$ and $PSVS_{3.8}$, the content of iodinated VSt is 23.1 and 3.2 mol%, respectively. They are termed as $PSVSI_{23.1}$ and $PSVSI_{3.2}$, respectively. The $PSVSI_x$ with different iodinated degree exhibits a single and symmetrical peak, and the molecular weight distribution (M_w/M_n) is narrow (Fig. 2a). The SEC-MALLS results for $PSVSI_{23.1}$ and $PSVSI_{3.2}$ are summarized in Table 1.

3.3. Synthesis of the graft copolymers PSVS-g-PS

PSLi with two different lengths are synthesized first. The number-averaged molecular weight of the two side chains ($M_{n,br}$) are 9.9 and 23.4 kg/mol (Table 1, they are termed as PS9.9 and PS23.4, respectively). Four PSVS-*g*-PS samples with different molecular parameters are synthesized by the nucleophilic substitution reaction between $PSVSI_x$ ($PSVSI_{23.1}$ and $PSVSI_{3.2}$) and PSLi (PS9.9 and PS23.4). In the denomination of PSVS-*g*-PS samples in Table 1, the backbones PSVS45.3 and PSVS54.4 represent $PSVS_{31.4}$ and $PSVS_{3.8}$, respectively. In order to obtain the pure comb polymers, the resultant products need to be precipitation–fractionation. In Fig. 1c, the peak at 3.2 ppm (corresponding to the $-CH_2CH_2CH_2C\mathbf{H_2}I$) disappears completely in the ^{1}H NMR spectrum of PSVS45.3-18.9-PS23.4, implying the full reaction of iodine atom of $PSVSI_{23.1}$ with PSLi. The molecular weights of the comb-like copolymers are characterized by SEC-MALLS (Table 1). The typical SEC trace of fractionated PSVS-*g*-PS is shown in Fig. 2b. It is observed that the comb-like copolymers (PSVS-*g*-PS) with narrow molecular distribution are successfully synthesized. The branching density, which is the number of branch chains per 100 repeat units of the backbone of graft copolymers, can be calculated by $\{[(M_{n,comb} - M_{n,bb})/M_{n,br}]/(M_{n,bb}/M_{bb})\} \times 100\%$, where $M_{n,comb}$, $M_{n,bb}$ and $M_{n,br}$ are the number-averaged molecular weights for the graft copolymer, backbone and side chain, respectively, and M_{bb} is the molecular weight of the repeat unit of the backbone [16]. From the above results, the average number of branch chain per backbone (n_{br}) and the volume fraction of the branches (ϕ_{br}) are also calculated (Table 1).

The entangled molecular weight (M_e) of PS melt is reported to be 17.3 kg/mol [68]. The synthesized comb-like copolymers have branches below or above M_e ($M_{n,br}/M_e$ ranges from 0.6 to 1.4), while

the backbone is slightly entangled ($M_{n,bb}/M_e$ ranges from 2.6 to 3.2). The average number of the C atom (q) and the number average weight of the segment (M_s) between two adjacent branch chains are also calculated to better understand the structure of the comb-like copolymers. For PSVS54.4-2.4-PS9.9 and PSVS54.4-2.5-PS23.4, q and M_s are 80 and 4160 g/mol, respectively. For PSVS45.3-20.7-PS9.9 and PSVS45.3-18.9-PS23.4, q and M_s are about 10 and 510 g/mol, respectively. It is apparent that the comb-like copolymers have small segment between two adjacent branch chains in the backbone.

3.4. Glass transition temperature (T_g) of the comb polymers

Glass transition temperature (T_g) of the resultant samples was analyzed by means of DSC measurements. The influence of branch chain on melt behavior was also reflected in the transition from glassy (or amorphous) state to melt state, i.e. glass transition process. Comb-like PSVS-*g*-PS has the amorphous backbone and side chains. Fig. 3 shows DSC second heating curves of linear PSVS, side chain PS, and graft copolymer PSVS-*g*-PS, and the results are summarized in Table 1. The T_g is the initial temperature at which polymer chain segment could move freely. The T_g of the backbone $PSVS_{31.4}$ (68.4 °C) is much lower than that of $PSVS_{3.8}$ (89.8 °C), the reason is that flexible short side chains (such as butenyl group) could greatly increase the movement ability of chain segment. The T_g of PSVS-*g*-PS copolymers is higher than those of both the backbone and side chains, which might result from reduced movement ability of chain segment due to the restriction of surrounded side-chain. When the branching density of PS branch chain is 2.5%, the T_g of PSVS54.4-2.5-PS23.4 (104.8 °C) is higher than that of PSVS54.4-2.4-PS9.9 (101.0 °C). This phenomenon is understandable if one considers the chain end effect of PS branches through the excess free volume around the chain ends [60]. The number of the chain end per unit molecular weight reduces with the increase of branch length. However, when the side chain is the same, the T_g is similar among the graft copolymers with different graft densities. The reason for this phenomenon needs to be further investigated.

3.5. Linear rheological property of PSVS-g-PS

In order to study how the presence of branch chains with high branching density (different from bottlebrush polymers) affects the linear rheological properties of comb-like polymers, the rheological properties of the resultant comb-like PSVS-*g*-PS are studied by the linear frequency sweep. Here the synthesized comb-like copolymers have branches below or above M_e ($M_{n,br}/M_e$ ranges from 0.6 to 1.4), while the molecular weight of backbone is higher than Me ($M_{n,bb}/M_e$ ranges from 2.6 to 3.2). Figs. 4 and 5 shows the master curves of the storage modulus (G') and loss modulus (G'') for the PSVS-*g*-PS samples, constructed at a reference temperature of 150 °C. As shown in Fig. 4a and b, when the length of branch chain is fixed as 9.9k (lower than the M_e of PS), G' as well as G'' of PSVS54.4-2.4-PS9.9 and PSVS45.3-20.7-PS9.9 decreases from the glass transition zone and goes to the terminal zone with decrease in the frequency, and there is no clear rubbery plateau region. However, the curves show two transition regions: one is the weak transition in the intermediate region (down-arrow), the other is the clear transition in the terminal regions (up-arrow), meaning two relaxation processes after glass transition region. The two-step relaxation of G' after glass transition region was reported to the fast motion of the branch in the intermediate frequency region and the slow motion of the main chain in the terminal frequency region [57, 62, 64]. When the length of branch chain is increased to 23.4k (higher than the M_e of PS, but lower than the critical molecular weight ($M_c = 2M_e$) of PS), the appearance of the plateau region ($G' > G''$) in the intermediate frequency region indicates the elastic nature in the PSVS54.4-2.5-PS23.4 and PSVS45.3-18.9-PS23.4 melts (Fig. 5), suggesting some kinds of chain entanglement between the side chains in the comb-like PSVS-*g*-PS. Tsukahara et al. [60] found a similar phenomenon in the poly(macromonomer)s. They thought that the topological factor related to the multibranched structure might influence the chain entanglement by increasing the relaxation time of branch chains for the unentanglement. Moreover, it is also possible that the branching structure of the

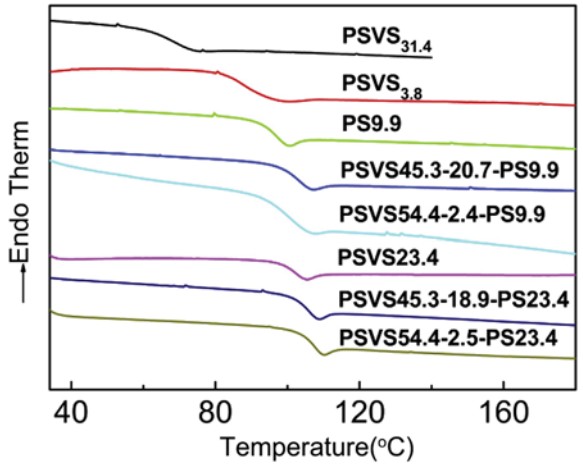


Fig. 3. DSC heating curves of linear PSVS, side chain PS, and comb polymers (PSVS-*g*-PS).

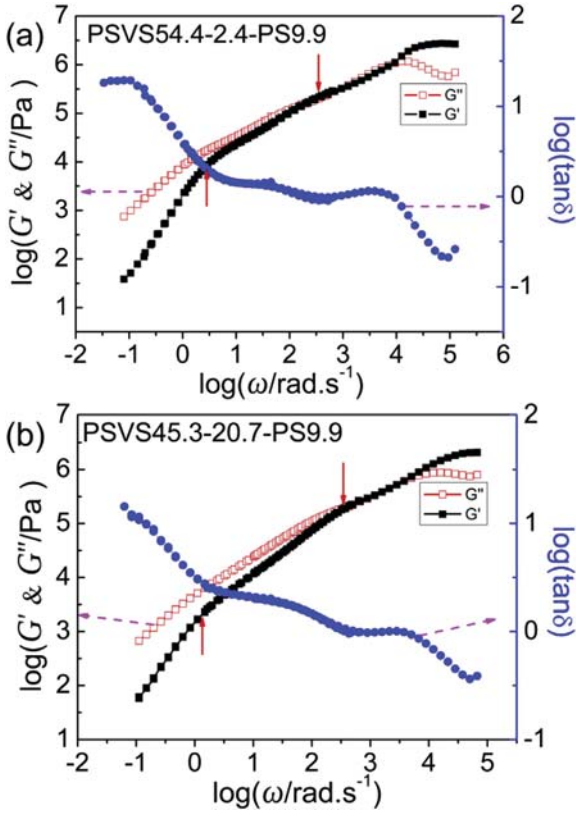


Fig. 4. Master curves of storage moduli (G'), loss moduli (G''), and tan δ versus angular frequency (ω) for the comb-like copolymers: (a) PSVS54.4-2.4-PS9.9 and (b) PSVS45.3-20.7-PS9.9 at the reference temperature of 150 °C. Arrows represent the transition points in transition regions.

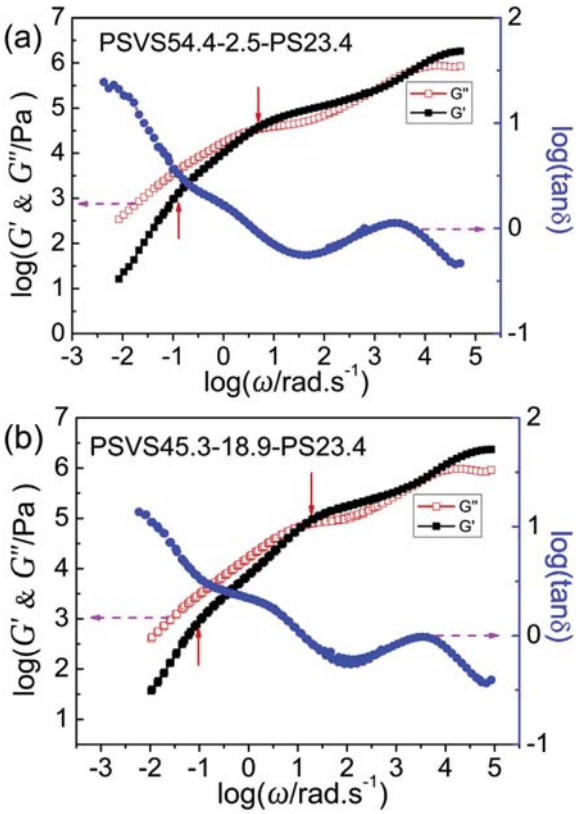


Fig. 5. Master curves of storage moduli (G'), loss moduli (G'') and tan δ versus angular frequency (ω) for the comb-like copolymers: (a) PSVS54.4-2.5-PS23.4 and (b) PSVS45.3-18.9-PS23.4 at the reference temperature of 150 °C. Arrows represent the transition points in transition regions.

poly(macromonomer)s influences the $M_c = 2M_e$ relationship known for the conventional linear polymers.

It is expected that branched polymers should relax sequentially. The chain segments should relax first, followed by the side chains, and the whole polymer should be the last to move [69,70]. To clarify the attribution of two relaxations in the dynamic spectrum for comb-like polymers with different length of branch chain, the plot of tan δ versus angular frequency (ω) for the comb-like copolymers is also shown in Figs. 4 and 5. In Figs. 4 and 5, the minimum of tan δ (δ is the phase angle) in the intermediate frequency region is observed for all four samples, which is thought to be related with branch relaxation [36,56,57]. At the same time, there is apparent shoulder transition for tan δ versus ω in low angular frequency region, which is often inferred to be associated with the backbone relaxation [36,56,57]. Considering high branching density of branch chain and the low effective concentration of the backbone in the PSVS-*g*-PS samples, it is difficult for the backbones from different comb-like copolymers to contact each other, so we think that the shoulder transition for tan δ versus ω in low angular frequency region in this work may result from that the relaxation of whole comb-like copolymer [61,63].

Some previous reports [54,71] have shown that in order to simplify the analysis about the relationship between the modulus and the molecular weight of relaxation unit, the behavior of comb-like polymers with short branches may be thought to be similar to that of short multiarm star-like polymers. According to the Rouse theory or the Rouse-Ham theory for star chains [72,73], the value of modulus of the slowest mode of linear chains or the branch of star polymers is related to the molecular weight, maybe described as $G' = \rho RT/M$. Here, ρ, R and T are the density, gas constant and temperature, respectively. The G'_{br} and G'_{total} represent the storage moduli in the intermediate frequency region (originated from the relaxation process of the branches) and the terminal frequency region (originated from the relaxation process of the whole comb-like copolymer). We used two methods to determine the values of G'_{br} and G'_{total} (Fig. 6). The first method is based on the curve of tan δ with ω, that is, the storage modulus corresponding to the minimum of tan δ (in the intermediate frequency region) is used as the $G'_{br,1}$, and the storage modulus corresponding to the shoulder transition for tan δ versus ω (in the terminal frequency region) is used as $G'_{total,1}$; the second is based on the direct determination of storage modulus for G'_{br} and G'_{total} at the two inflexions on the G' curve versus ω, the determined G'_{br} and G'_{total} are defined as $G'_{br,2}$ and $G'_{total,2}$, respectively.

Table 2 presents storage modulus G' in the intermediate and terminal regions from the master curves and calculated G' by the equation $G' = \rho RT/M$ based on the M_n measured by SEC-MALLS. For all four comb-like copolymers, the calculated G'_{br} (PS9.9 or PS23.4) is higher than the experimental value of G'_{br} in spite of using method 1 or 2. This result implies that the relaxation in the intermediate region does not reflect the motion of the single branch chain and strongly suggest the cooperative motion of more than 2 branch chains. Iwawaki et al. suggested that there was the cooperative motion of side chains in bottlebrush-like PS, originating from the repulsive interaction between the branches [71]. At the same time, the calculated G'_{total} is also higher than the experimental value of G'_{total} in spite of using method 1 or 2. This result maybe mean that the relaxation in the terminal region (within measured frequency region) does not reflect the motion of single whole comb-like polymer and strongly suggest the cooperative motion of more than 2 comb-like polymers. According to the results from experiments and Monte Carlo simulations, the authors found a slow terminal relaxation process in the star-like polymers with a large number of arms, in addition to the classical faster arm retraction mechanism, which was attributed to translational cooperative rearrangements of the stars [74,75]. On the other hand, for the comb PS with less than 100 branch chains per 10,000 carbon atom of the backbone, we found that the calculated storage modulus (G'_{br} and G'_{bb}) (here the branch density is about 57 branches per 10,000 carbon atom of the backbone [47]) is similar to the storage modulus from the direct determination of storage modulus for G' at the two inflexions on the G' curve versus ω ($G'_{br,2}$ and $G'_{bb,2}$) (in Table S1 in the Supporting Information). In other words, the intermediate transition and the terminal transition come from the side chain relaxation and the backbone relaxation, respectively. At the same time, both the branch relaxation and the backbone relaxation do not show cooperative effect.

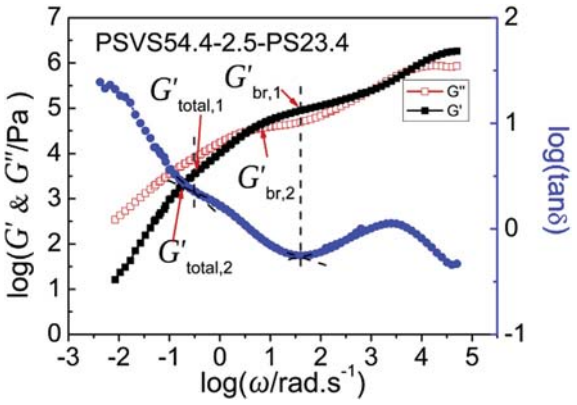


Fig. 6. G'_{br} and G'_{total} for the comb-like copolymer PSVS54.4-2.5-PS23.4.

Table 2
Comparison of calculated G' with the obtained G' from the G' curve versus ω.

Sample	G'[a] (kPa)	G' (kPa)			
		$G'_{br,1}$[b]	$G'_{total,1}$[b]	$G'_{br,2}$[c]	$G'_{total,2}$[c]
PS9.9	373.0				
PS23.4	157.8				
PSVS54.4-2.4-PS9.9	23.9	207.5	13.3	228.7	8.8
PSVS54.4-2.5-PS23.4	11.9	92.5	3.4	37.8	4.1
PSVS45.3-20.7-PS9.9	5.4	219.3	2.6	190.4	2.3
PSVS45.3-18.9-PS23.4	2.5	165.7	1.5	72.2	0.8

[a] Calculated by the equation $G' = \rho RT/M$ based on the M_n obtained by SEC-MALLS.
[b] The storage modulus G' corresponding to the minimum or shoulder transition point of tan δ.
[c] Based on the direct determination of storage modulus for G' at the two inflexions on the G' curve versus ω.

Fig. 7a shows the plot of the complex viscosity (η^*) versus frequency (ω). It is observed that the value η^* in the Newtonian regime of the complex viscosity increases with the length of branch chains when the branching density is fixed. The zero shear viscosity (η_0) of sample is obtained from the Newtonian regime of the η^* versus frequency [65]. Fig. 7b presents the influence of the molecular weight on the η_0 of PSVS-*g*-PS. As we know, the M_w of PSVS-*g*-PS will increase with the increase of branching density or branch length. When the molecular weight of branch chain is 9.9 kg/mol, the η_0 of PSVS-*g*-PS melt slightly decreases with the increase of branching degree. When the branch chain length is 23.4 kg/mol, the η_0 of PSVS-*g*-PS melt keeps almost the same with the increase of branching degree. This phenomenon might be explained by dynamic dilution concept [76,77]. The retracted branches act as an effective solvent, leading to a swelling of the backbone. So the η_0 decreases or almost keeps the same with the increase of branching degree, although the M_w of the whole comb-like polymer is

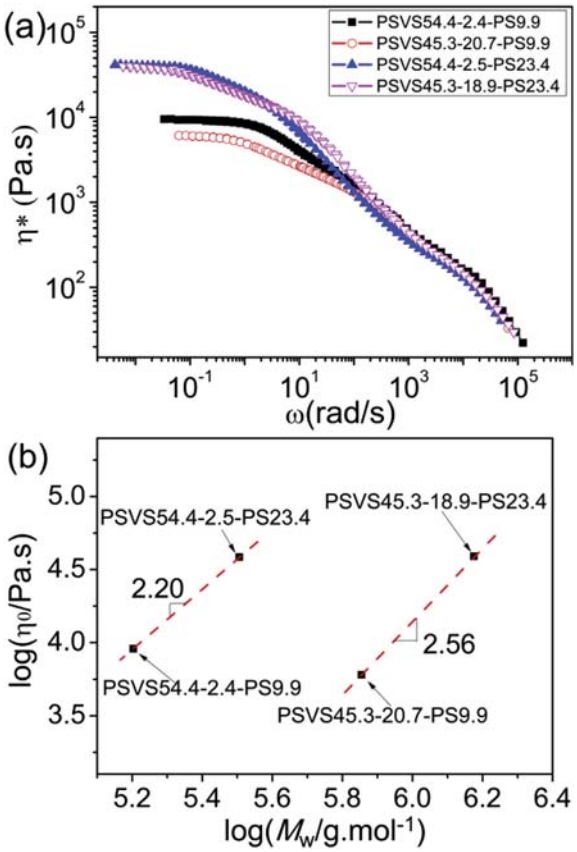


Fig. 7. (a) The η^* versus ω and (b) the η_0 versus M_w for the comb polymers.

increased. When the branching density is fixed, in spite of low or high branching density, it is observed that the η_0 of PSVS-*g*-PS melt follows a power law dependence on molar mass, approximately described by $\eta_0 \sim M_w^{\alpha}$, $\alpha \approx 2.2-2.6$, although there is no enough data for this power law relationship. Interestingly we compare the results with the comb-like PS with less than 100 branches per 10,000 carbon atom of the backbone. According to the Ref. [47], when the molecular weight of the branch chains is higher than the M_c, the η_0 of comb PS with about 57 branches per 10,000 carbon atom of the backbone melt follows a power law dependence on molar mass, $\alpha \approx 2.9$, which is very close to the case of well entangled linear polymer chains (Fig. S2 in the Supporting Information). Generally, for linear polymers below M_e, the viscosity obeys the Rouse model prediction, i.e., $\alpha = 1$. However, a sharp increase in the power law exponent occurs above M_c due to the onset of entanglements. An empirical value of $\alpha = 3.4$ describes the scaling of well-entangled melts above M_c [65,78]. In contrast, the recent report shows that the value of α for poly(macromonomers) (or bottlebrush) with very big molecular weight can still be approaching to 1 [65], dynamically similar to unentangled linear polymer chains. Considering the molecular architecture and branching density of PSVS-*g*-PS, and $\alpha \approx 2.2-2.6$, there is some degree of entanglement but not well entangled in the PSVS-*g*-PS, which is different from melt behavior of both poly(macromonomers) and well entangled linear polymer chains.

4. Conclusions

A series of model comb-like polymers PSVS-*g*-PS have been successfully synthesized based on living anionic polymerization and hydrozirconation reaction. It is a facile way for modular synthesis of comb polymers by nucleophilic substitution reaction between iodinated poly (St-*co*-VSt) ($PSVSI_x$, backbone) and living polymer lithium (PSLi, side chain). Tunable molecular weight of PSVS-*g*-PS with narrow molecular weight distribution could be obtained by changing the length and branching density of branch chain. The synthesized comb-like copolymers with high branching degree have branches below or above M_e ($M_{n,br}/M_e$ ranges from 0.6 to 1.4), while the molecular weight of backbone is larger than M_e ($M_{n,bb}/M_e$ ranges from 2.6 to 3.2).

The results from the linear rheological properties of the PSVS-*g*-PS showed hierarchical relaxation process. After the glass transition region, one is in the intermediate region and corresponds to the relaxation of the side chain; the other is in the terminal region and is related to the movement of the whole comb polymer. Furthermore, the increasing in the branch chain length causes the branch chains to entangle intermolecularly. From the η_0 of PSVS-*g*-PS, we can see that the melt behaviour of PSVS-*g*-PS is different from both poly(-macromonomers) and entangled linear polymer chains. It is hoped that the experimental research in this study would stimulate the theoretical or simulation work for the linear rheology of the comb-like graft copolymers with high branching density of branch chain.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.01.020.

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